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A Reexamination of ^{19}F NMR in Selected Solids,
The Conductor Ag_2F and Reference Insulators for
Studies of $YBa_2Cu_3O_7$-Type Superconductors

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NMR signals of ^{19}F have been measured in the polycrystalline inorganic conductor Ag_2F and in the polycrystalline insulators AgF, YOF, $EuOF$, YF_3, CuF_2, BaF_2 and KF to compare them to the signals found in the so-called "1-2-3-type" compounds with claimed formulas $RBa_2Cu_3O_{7-x}F_x$ ($R=Y$ and Eu). No evidence for a Knight-shifted, built-in fluorine-signal was found in the 1-2-3-type superconductors, whereas Ag_2F shows a clearly downfield shifted ^{19}F peak with reference to AgF.

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1

A REEXAMINATION OF ^{19}F NMR IN SELECTED SOLIDS,

THE CONDUCTOR Ag$_2$F AND REFERENCE INSULATORS FOR

STUDIES OF YBa$_2$Cu$_3$O$_7$-TYPE SUPERCONDUCTORS[*]

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ABSTRACT

NMR signals of ^{19}F have been measured in the polycrystalline inorganic conductor Ag_2F and in the polycrystalline insulators AgF, YOF, EuOF, YF_3, CuF_2, BaF_2 and KF to compare them to the signals found in the so-called "1-2-3-type" compounds with claimed formulas $RBa_2Cu_3O_{7-x}F_x$ (R=Y and Eu). No evidence for a Knight-shifted, built-in fluorine-signal was found in the 1-2-3-type superconductors, whereas Ag_2F shows a clearly downfield shifted ^{19}F peak with reference to AgF.

INTRODUCTION

Evidence of incorporated F in the so called "1-2-3-type", $YBa_2Cu_3O_7$-derived compounds has been cited[1-5]. The aim was to confirm an increase in T_c as Ovshinsky[6] claimed in 1987 by substitution of F for O. One expects for the 1-2-3-type compounds, since they display metallic conductivity at room temperature, a downfield-shifted F NMR resonance (compare: ^{17}O NMR shifts[7]). As a guideline for judging the line positions and shapes of fluorine incorporated in the 1-2-3-type compounds, we therefore reexamined the ^{19}F NMR signals in a metallic inorganic conductor(Ag_2F), in the insulating starting materials used to synthesize the superconductor phases(YOF, $EuOF$ and YF_3) and in BaF_2 and CuF_2 which could be formed during the synthesis. AgF and KF were used as reference samples. There appear to be only two inorganic compounds containing fluorine and showing high metallic conductivity:(1) Silver subfluoride[8], Ag_2F, with NMR results reported by Nishihara et al.[9] and (2) $(Ag_7O_8)^+(HF_2)^-$ reported by Hindermann[10]. Pulsed NMR of ^{19}F in solids has been reported by Vaughan et al.[11] and more recently by Clark et al.[12]. A number of results by CW ^{19}F NMR on anhydrous and hydrated forms of AgF [13], on YF_3 and also on BaF_2 and KF have been reviewed by Gabuda and Zemskov[14].

EXPERIMENTAL

A. Sample Preparation and Characterization

All samples, except Ag_2F and AgF, were prepared as follows[4]:
YOF and EuOF were obtained by reacting equimolar amounts of YF_3
(Reacton,99.99%), EuF_3 (Reacton,99.9%) and Y_2O_3(Reacton,99.9%) or Eu_2O_3
(Lindsay Chemicals), respectively, at $650°C$ for 18h in an alumina
combustion boat in air. The oxyfluoride products were pure according to
X-ray powder diffraction. The "$RBa_2Cu_3O_{7-x}F_x$" samples were synthesized
by reacting ROF (R=Y,Eu) with $2BaCO_3$ (Mallinckrodt) and 3CuO (Matthey)
in alumina combustion boats in air using heating and cooling regimes
similar to those used to prepare high quality $YBa_2Cu_3O_7$[15]. In each case
the major component was a $YBa_2Cu_3O_7$-like phase and BaF_2 as a minor
component. CuO and R_2O_3 were sometimes detectable by X-ray diffraction.
Samples of "$RBa_2Cu_3O_{7-x}F_x$" containing the least amount of BaF_2 were
prepared by reacting ROF(R=Y, Eu) and $BaCO_3$ in two heating cycles with
intermediate grinding: $800°C$ for 12h, and $875-900°C$ for 10h followed by
cooling in 8h to room temperature. A semiquantitative X-ray diffraction
analysis was carried out as follows: Mixtures of BaF_2, CuO, Y_2O_3 and
$YBa_2Cu_3O_7$ in relative amounts corresponding to the products which would
have been obtained assuming (I) complete conversion of the reactant
fluoride to BaF_2 and (II) 50% conversion of reactant fluoride to BaF_2
were mixed and heated in the same way as the "$RBa_2Cu_3O_{7-x}F_x$"samples. The
relative intensities of the diffraction peaks at d= 3.58 Å, the
strongest line in the pattern of BaF_2 , were compared in these mixtures
with those of the $YBa_2Cu_3O_{7-x}F_x$-like phases in order to estimate x.

These results were consistent with a partial incorporation on the order of 0.2 mole of F per Mol of host. Incorporation of some fluoride in the 1-2-3-type lattice was also indicated by changes in the unit cells and iodometric analyses of average copper oxidation states[4]. The "$RBa_2Cu_3O_{7-x}F_x$"samples displayed superconducting transitions in the magnetic susceptibility versus temperature curves occuring 20-25 K lower than the reported values for $YBa_2Cu_3O_{7-\delta}$. The transition ranges are also broader and show a much weaker Meissner effect.

AgF, 99.9%, with some content of $AgF.(H_2O)_x$, and $KF.2H_2O$ were both obtained from Aldrich Chemicals. Ag_2F was prepared by the method of L.Poyer et al.[16] ,suggested by R.E.McCarley, Ames Laboratory and Department of Chemistry, Iowa State University. The X-ray powder diffraction patterns of Ag_2F agreed with published data[17].

B. NMR Measurements

Pulsed NMR measurements were performed on a homebuilt ^{19}F NMR probe, with the double bearing version rotors of Wind's design [18], capable of spinning up to more than 7 KHz, in a Bruker MSL-300, operated at a frequency of 282.2 MHz, and with a 90° pulse of 2 µs duration. Fluorine-free spinner materials used were either polycarbonate or Araldite (Ciba-Geigy Ltd.,Basel,Switzerland); Torlon (DuPont) was found to contain F.

Transient techniques in NMR included: (1) single pulse excitation, either static or with Magic Angle Spinning (MAS), (2) spin echo as Spin Echo Envelope Mapping (SEEM). SEEM involves 90_x-τ-180_y and Fourier-Transformation from the center of the echo. It is applied to obtain the

line shape of wide lines. By increasing the RF frequency, with re-tuning

of the probe for each new frequency, in steps from values smaller than

the center-frequency to larger values, a series of spectra are

obtained; the envelope of these signals map the envelope of the broad

NMR line.(3) static Multi-Pulse-Dipolar-Decoupling (MPD) or (4) CRAMPS,

Combined Rotation and Multi-Pulse Decoupling using the MREV-8

sequence[19], with cycle time t_c=48 μs.

RESULTS

Table 1 shows the present results compared to previously reported

data. Because the shift values were measured against C_6F_6, i.e.

$\delta(C_6F_6)$=0, most of the earlier results had to be converted to this

reference. Earlier papers results are referred mostly to $\delta(F_2)$=0 ,the so

called "Absolute Fluorine Scale". The resonance of F_2 gas lies very far

downfield compared to C_6F_6. So, to convert the data of the present work

to the shift region around $\delta(C_6F_6)$ requires subtractions of large

numbers. For the present work $\delta(C_6F_6)$ - $\delta(F_2)$ was taken to be -585.8

ppm[20]. This fact and the relatively large uncertainties of the CW data,

mainly in earlier Russian work, explain some of the smaller

discrepancies reported in Table 1.

The present results for Ag_2F and AgF lie far outside of these

conversion errors. The isotropic shifts differ by a factor of about 1.5

from the published data[9,21]. The reference AgF, supposedly of a

white(to lightly yellowish) color[22] was supplied by Aldrich Chemicals

as an orange-brown material. Ag_2F and AgF were both sealed in the

polycarbonate NMR spinner under dry nitrogen in the absence of light. In the AgF sample ,not surprisingly, therefore, instead of one, there were two well defined signals, one with high intensity at -150 ppm and a less intense peak at +38 ppm. The latter signal was assigned to the brown, hydrated form of silver fluoride, probably $AgF(H_2O)_x$ (x=2?)[22]. This assumption was confirmed by the fact, that after drying 24h in vacuum at 140°C the peak at 38 ppm had disappeared[**]. The high intensity peak remained, with a slight downfield shift (at most 5 ppm) and is therefore assigned to water-free AgF.

The present results on BaF_2 agree with those of Vaughan[11a] and of Burum[11b] to within experimental error, whereas the older Russian CW work shows large deviations from these results. The signal of YOF under MPD shows an axial shielding tensor with principal values of $\sigma_\perp$= 110±5 ppm and $\sigma_\parallel$=37±5ppm (table 1). The EuOF shows a very large paramagnetic shift and could only be reasonably detected by the method of Spin-Echo-

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**) During drying at 140°C the reaction $2AgF+H_2O=Ag_2O+2HF$ takes place and therefore the sample darkens. But HF seems not to react to form $Ag^+(FHF)^-$ since after drying, the lineshape showed no sign of a wide doublet as expected from a comparison measurement with $K^+(FHF)^-$. The water remaining in the sample of AgF after drying was only a few percent of the amount originally present in the fresh commercial sample. This fact was checked by proton NMR.

Envelop-mapping(SEEM). The measured linewidth is 800±50ppm. For YF_3

static MPD resulted in resolving the components of the asymmetric

shielding tensor to be $\sigma_{11}=140$ppm, $\sigma_{22}=108$ppm and $\sigma_{33}=82$ppm. The

calculated value of $\bar{\sigma}$ compares quite well with the measured one

considering the errors of both measurement and the remarks given in the

discussion (see table 1). The only earlier measurement of the chemical

shift powder pattern,known to the authors, is given in a paper by Gabuda

et al.[23] with a value of $\bar{\sigma}$ differing significantly from the present

value. ^{19}F in CuF_2 also shows a paramagnetic shift and a linewidth of

290 ppm. The signal could only be detected by SEEM.

The present determination of the isotropic shift of dried KF agrees

with reference 11a, but more recent values[12] differ by some ppm,

probably on account of the recalculation from the $CFCl_3$-to the C_6F_6-

scale presently used. Aqueous KF solutions have been remeasured for

comparison. The measurements reported in references 9 and 21 used KF

solutions as reference. Also shown in earlier work is the concentration

dependence of δ in these solutions. Only at very high concentrations,

not used in the present work, a slight δ-decrease of about 2ppm is

reported[12,24].

DISCUSSION

The main difference of the present results compared to those published earlier is found in the much larger shift values reported in the present work for Ag_2F and AgF. A scale calibration error in the earlier work [9 and 21)] could explain the discrepancy. Therefore calculating the expected diamagnetic shift of Ag_2F as in [9)] the present data would yield the value of -55ppm(i.e. 195ppm-250ppm, where the latter number is the theoretically calculated Knight-shift in reference 9). Note however that the static signal of this sample is of a slightly asymmetric shape with a clearly indicated shoulder in the downfield direction (see figure 2). Within the limits of error, this asymmetry is interpreted as a small axial Knight shift anisotropy (see table 1). This assignment conforms to the axial arrangement of the nearest neighbors of the fluorine atoms in Ag_2F, which has the trigonal CdI_2 structure, $P3\bar{m}1$ (D_{3d}^3) [25a)].

The crystal structure of AgF is cubic and of the NaCl-type(Fm3m, O_h^5) and therefore shows an isotropic shift with symmetrical lineshape.

The YOF sample seems to be of the ordinary β-modification, crystallizing in the trigonal space group $R\bar{3}m(D_{3d}^5)$ with hexagonal axes[25)]. This symmetry is in agreement with the present work showing an axially symmetric chemical shift tensor. No indication of paired formation of fluorines[26)] was found.

In YF_3 the present determination of an asymmetric shielding tensor can be understood from the known crystal structure of this compound[25)], showing an orthorhombic lattice with space group Pnma (D_{2h}^{16}); the unit

cell contains 12 fluorine atoms, 4 of them occupy site (1) and the other 8 are positioned in a nonequivalent site (2). Each fluorine in site (1), F(1), is surrounded by 6 nearest atoms in a range of distances between 2.6 and 2.8Å; these are 5 F and 1 Y. At the second site (2), nonequivalent to site (1), each F(2) is surrounded quite differently: 2 Y lie very near, at 2.3Å and the 3 nearest F are at distances between 2.6 and 2.8Å. The local symmetry of both sites is nonaxial, but the F(2) sites would appear to be more highly anisotropic. On the other hand the unit cell contains twice as many F(2) atoms. Therefore it seems very probable to assign our observed σ anisotropy to the fluorines at the (2)-sites, the surroundings of the fluorines at the (1)-site appearing quasiisotropic. Furthermore the isotropic chemical shift of the two sites must be almost the same, since in CRAMPS only one peak is found within the limits of the resolution (2ppm).

CuF_2 is an antiferromagnetic compound being paramagnetic at room temperature. The observed line width is too large to infer any structural information from the spin echo lineshape. To the knowledge of the authors the only published NMR on CuF_2 has been in the region of the Neel temperature and below, in zero-field[27].

In spite of a careful search for fluorine incorporated in the 1-2-3-type superconductors, no indication of a positively shifted fluorine signal, nor any signal of residual starting material of the preparation (YOF, EuOF, YF_3) therein was found. The present results indicate that the only fluorine-signals found in the compounds "$RBa_2Cu_3O_{7-x}F_x$"[4] were small amounts of BaF_2, for R=Y: 5.10^{-1}, for R=Eu: $\sim 2.10^{-1}$ mol(BaF_2)/(1 mol host). This is in agreement qualitatively with our semiquantitative

X-Ray diffraction analysis. The quantity of F detected in BaF_2 is 25 times or 8 times the minimum amount of F detectable for R=Y or Eu, respectively, under the present experimental conditions. These detection limits are predicated upon detectability in the superconductor(in the normal state) being the same as in the insulators and in Ag_2F studied in this work.

12

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Index to the table:

a) Before drying, as delivered and handled under dry N_2 gas; Shielded against light.

b) After 24h of drying at 140°C, under vacuum (3×10^{-2} torr).

c) Not possible to remove H•••F coupling of water.

d) Resolution of peaks with MAS not possible.

e) KF•$2H_2O$ dried at 150°C.

f) δ is independent of concentration within the range 5-35% gKF/100ml solution (0.9-6M/L; secondary reference for Ag_2F and AgF).

g) Halfwith of Spin-Echo-Envelope obtained by appropriate frequency variation.

h) [9] and [21], wherein error values are cited.

i) [28]

K) [23] and [29], wherein error values are cited.

l) The fist data is cited in [14], the second is taken from fig.1 in [14].

m) [24] AgF in 1 molar aqueous solution; δ-shift converted from F_2-to C_6F_6-scale.

n) [11a]

o) [11b]

p) [23]

q) [30]

r) Are there pairs of fluorine in trigonal YOF?[26].

s) [23] and [30]

t) [12] KF dried at >100°C; MAS at 3KHz; Shift values converted from $CFCl_3$-to C_6F_6-scale with $\delta(CFCl_3)-\delta(C_6F_6)=162.9$ppm[20].

u) [24] Shift values converted F_2-to C_6F_6-scale with $\delta(F_2)-\delta(C_6F_6)$

=585.8ppm[20]; see also remarks under [1]; all converted shift

values suffer from this transformation and are therefore subject to

an error.

Captions to figures:

Figure 1: Ag_2F, $\delta\sim196ppm$, with MAS. The sample still contains small amounts of $AgF\bullet(H_2O)_x$, $\delta\sim41ppm$, and AgF, $\delta\sim-150ppm$, after preparation.

Figure 2: Anisotropic, static line pattern of the Knight-shifted Ag_2F, with $K_{\parallel}\sim228\pm5ppm$, $K_{\perp}\sim182\pm3ppm$.

Figure 3: AgF, $\delta\sim-149ppm$, "impurity" $AgF\bullet(H_2O)_x$, $\delta\sim37ppm$, with MAS, before drying the sample.
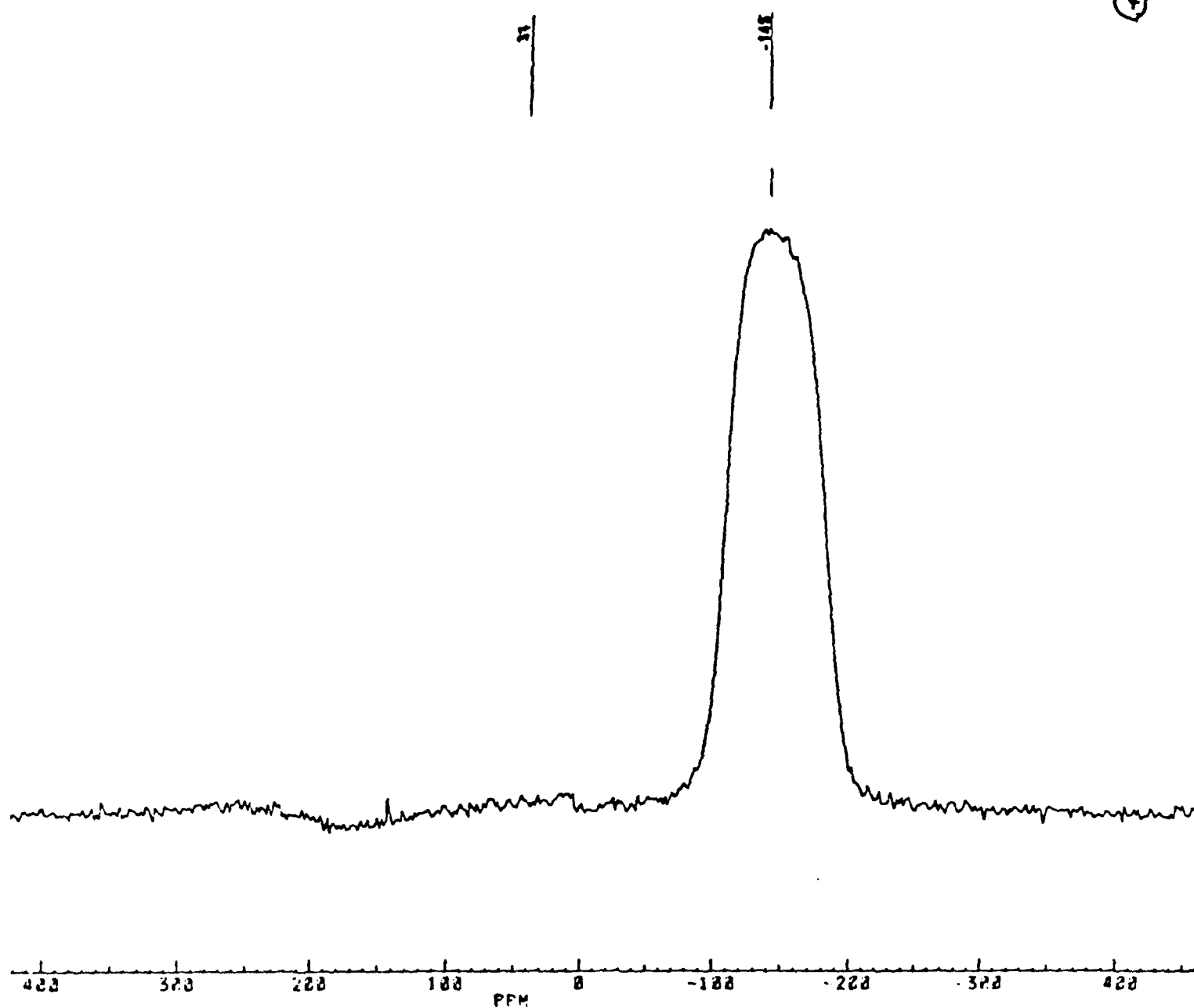
Figure 4: Static peak of AgF, $\delta\sim-145ppm$, after drying the sample shown in figure 3; the peak at $\delta\sim37$ ppm has disappeared.
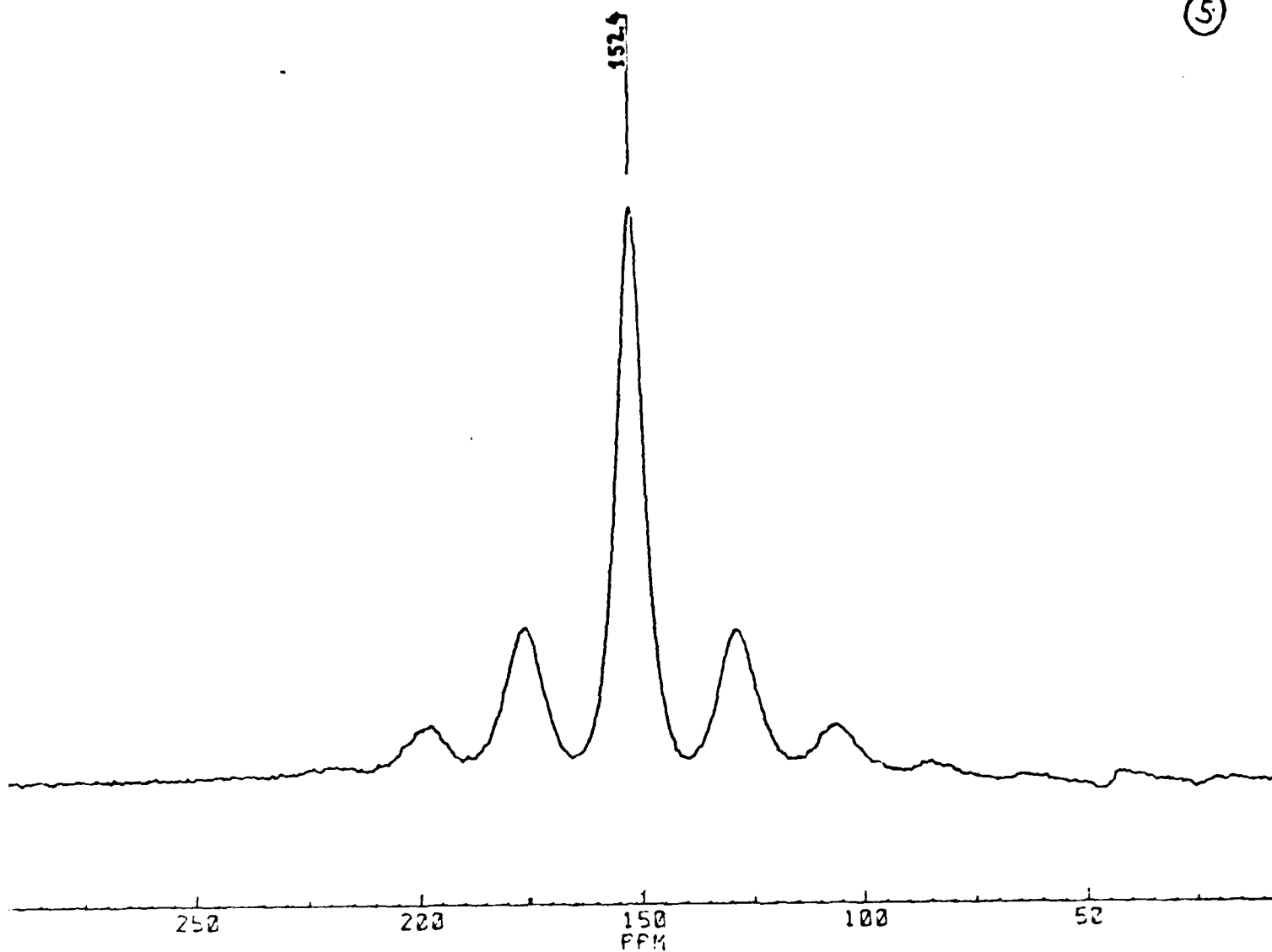
Figure 5: BaF_2, $\delta\sim152ppm$, with MAS and ~6.3 KHz spinning frequency.
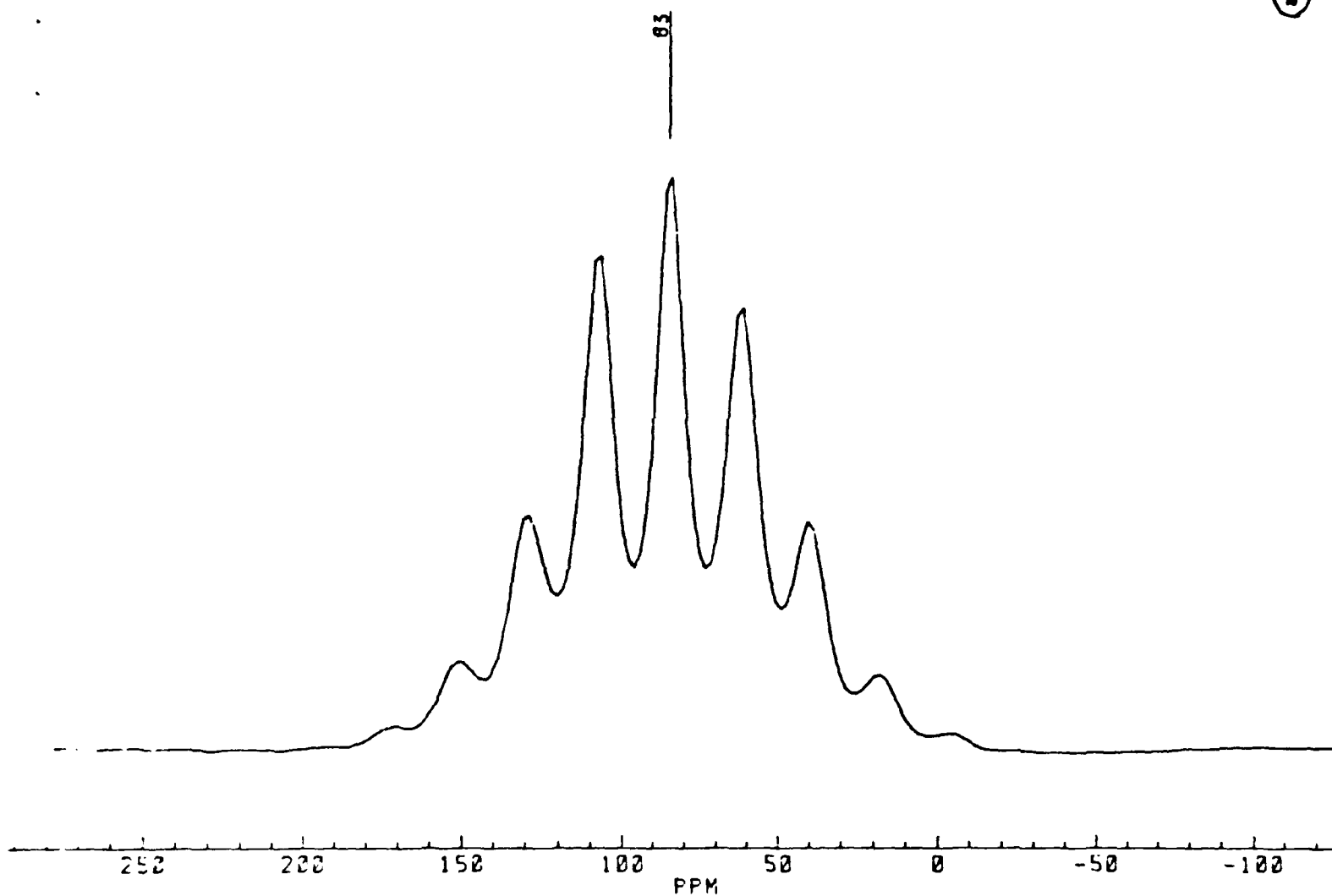
Figure 6: YOF, $\delta\sim83ppm$, with MAS.

Figure 7: EuOF with Static Spin-Echo Mapping.

Figure 8: Static MPD of YF_3; 3 peaks at $\sigma_{11}\sim140ppm$, $\sigma_{22}\sim108$, $\sigma_{33}\sim82ppm$.

Figure 9: CuF_2, $\delta\sim60ppm$, with Static Spin-Echo Mapping.

^{19}F Chemical Shifts and Linewidths in δ-:

COMPOUNDS	Single Pulse STATIC			Single Pulse MAS		Spin-Echo		Multipulse Decoupl STATIC		
	Peak Center	δ⊥	δ∥	Line-width	Center Peak	Peak center	Line-width	σ_{11}	σ_{22}	σ_{33}
Ag$_2$F	189 $^+_-$5	182 K⊥	228 K∥	68	197 $^+_-$2					
AgF$^{a)}$ AgF$^{b)}$	-153 $^+_-$3 -145 $^+_-$3			71 75	-149 $^+_-$1			≈150$^+_-$1	-150$^+_-$1	-150$^+_-$1
AgF·(H$_2$O)$_x$ (x=2?)	40 $^+_-$2			74	37 $^+_-$2			c)		
BaF$_2$	157 $^+_-$3			82	152 $^+_-$1			152$^+_-$1	152$^+_-$1	152$^+_-$1
YOF	84 $^+_-$5	σ⊥: 112 $^+_-$5	σ∥: 37 $^+_-$5	114	83 $^+_-$3			107$^+_-$3	107$^+_-$3	37$^+_-$3
EuGF	103$^+_-$15			183	d)	+460$^-_-$20	800 $^{g)}$			
YF$_3$								140$^+_-$3	108$^+_-$3	82$^+_-$3
CuF$_2$						+ 60$^+_-$10	290 $^{g)}$			
KF	37 $^+_-$3			49				35$^+_-$1	35$^+_-$1	35$^+_-$1
KF-Solution$^{f)}$	49 $^+_-$1									

F I G U R E ①

Ag_2F , $\delta \sim 196$ ppm , with MAS . The sample still contains

small amounts of $AgF.(H_2O)_x$, $\delta \sim 41$ ppm , and AgF, $\delta \sim -150$ ppm ,

after preparation .

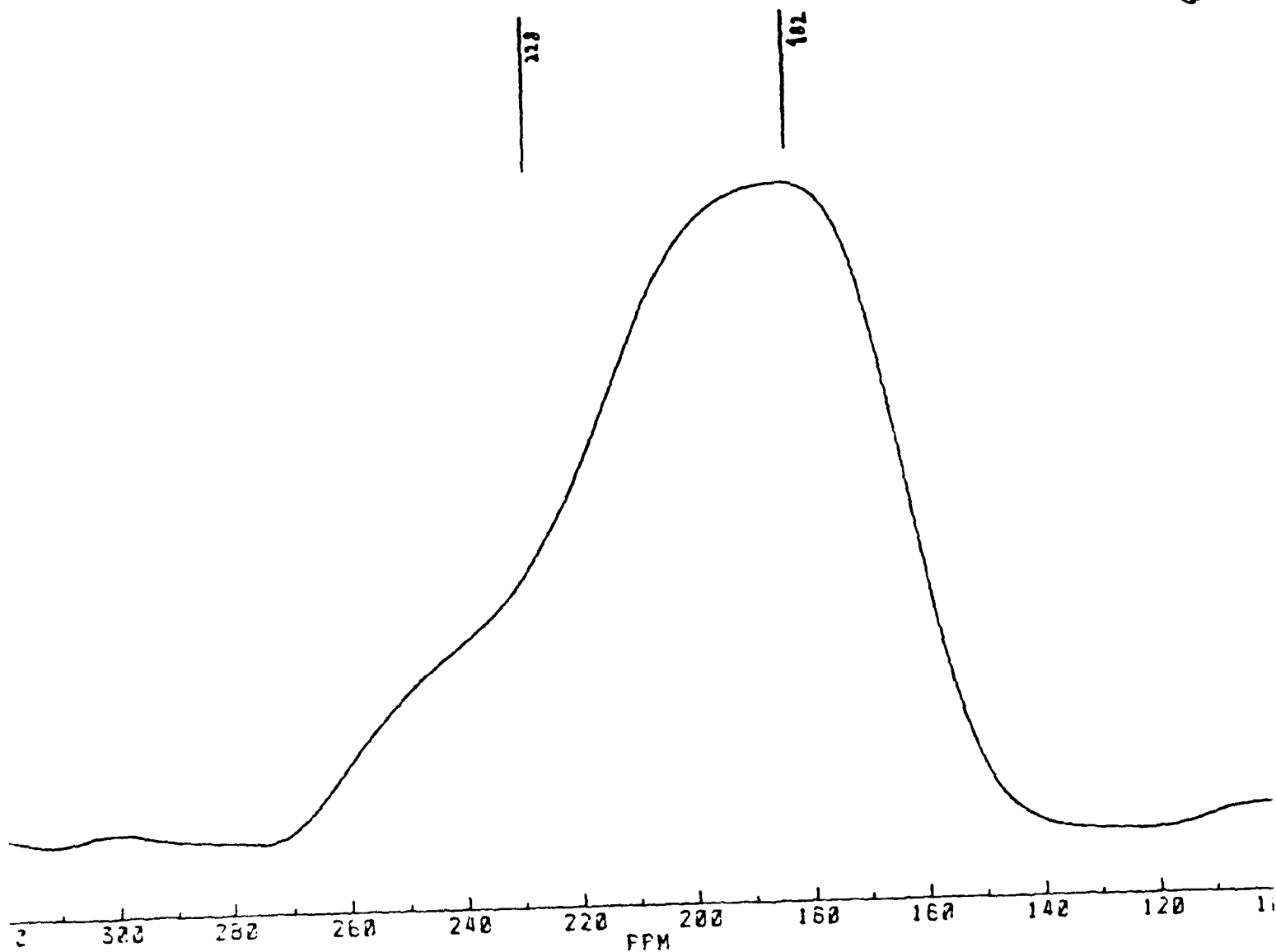FIGURE ②

Anisotropic, static line pattern of the Knight-Shifted Ag_2F .

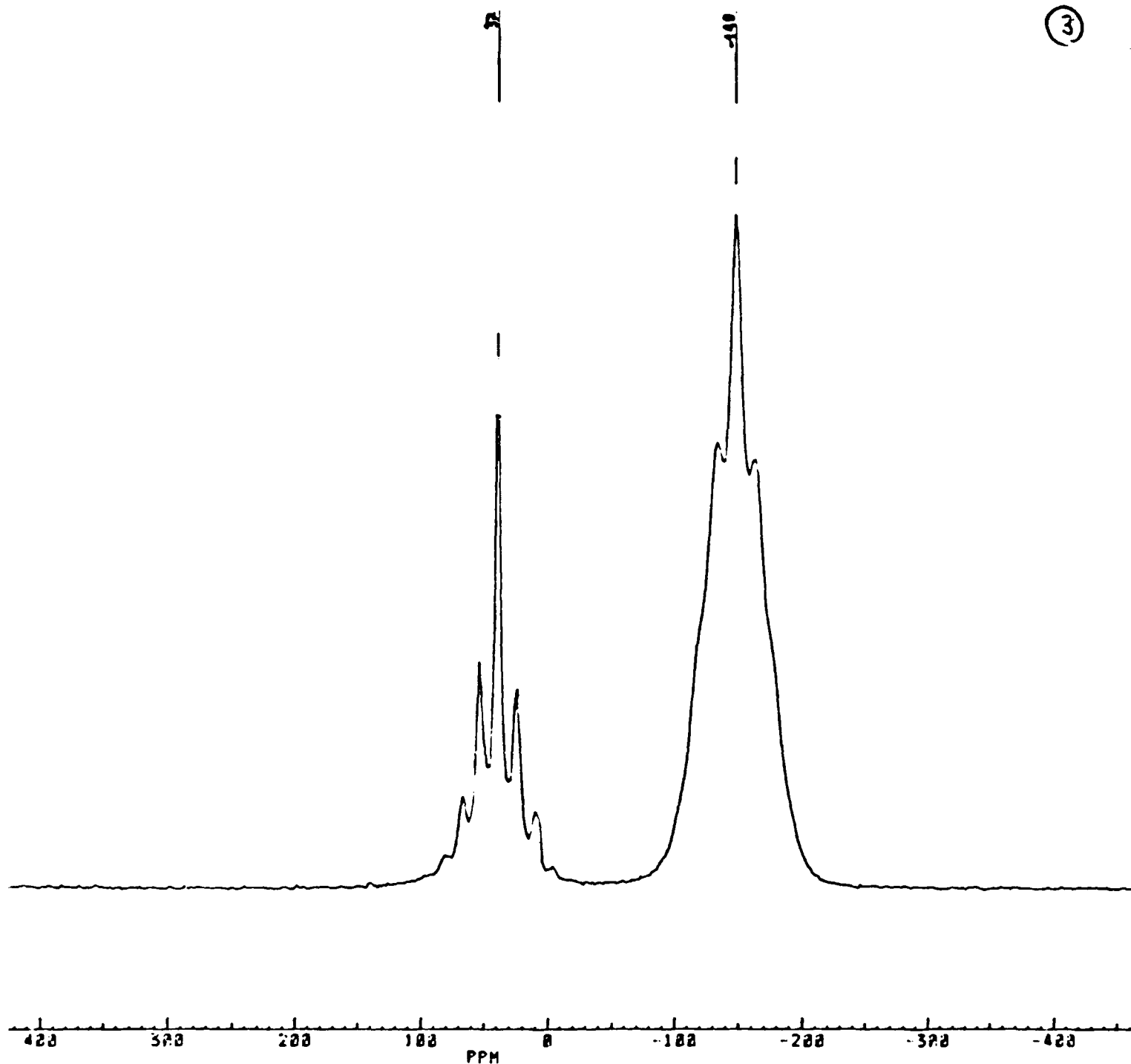with $K_{\shortparallel} \sim 228 \pm 5$ ppm , $K_{\perp} \sim 182 \pm 3$ ppm .

F I G U R E ③

AgF, δ ~ -149 ppm , + "impurity" AgF.$(H_2O)_x$, δ ~ 37 ppm ,

with MAS, before drying the sample .

F I G U R E ④

Static peak of AgF , δ ~ -145 ppm, after drying the sample

shown in figure ③ ; the peak at δ ~37 ppm has disappeared.

F I G U R E (5)

BaF$_2$, δ = 152.4 ppm , with MAS and ~6.3 KHz spinning frequency .

83

252   222   152   122   50   2   -50   -122
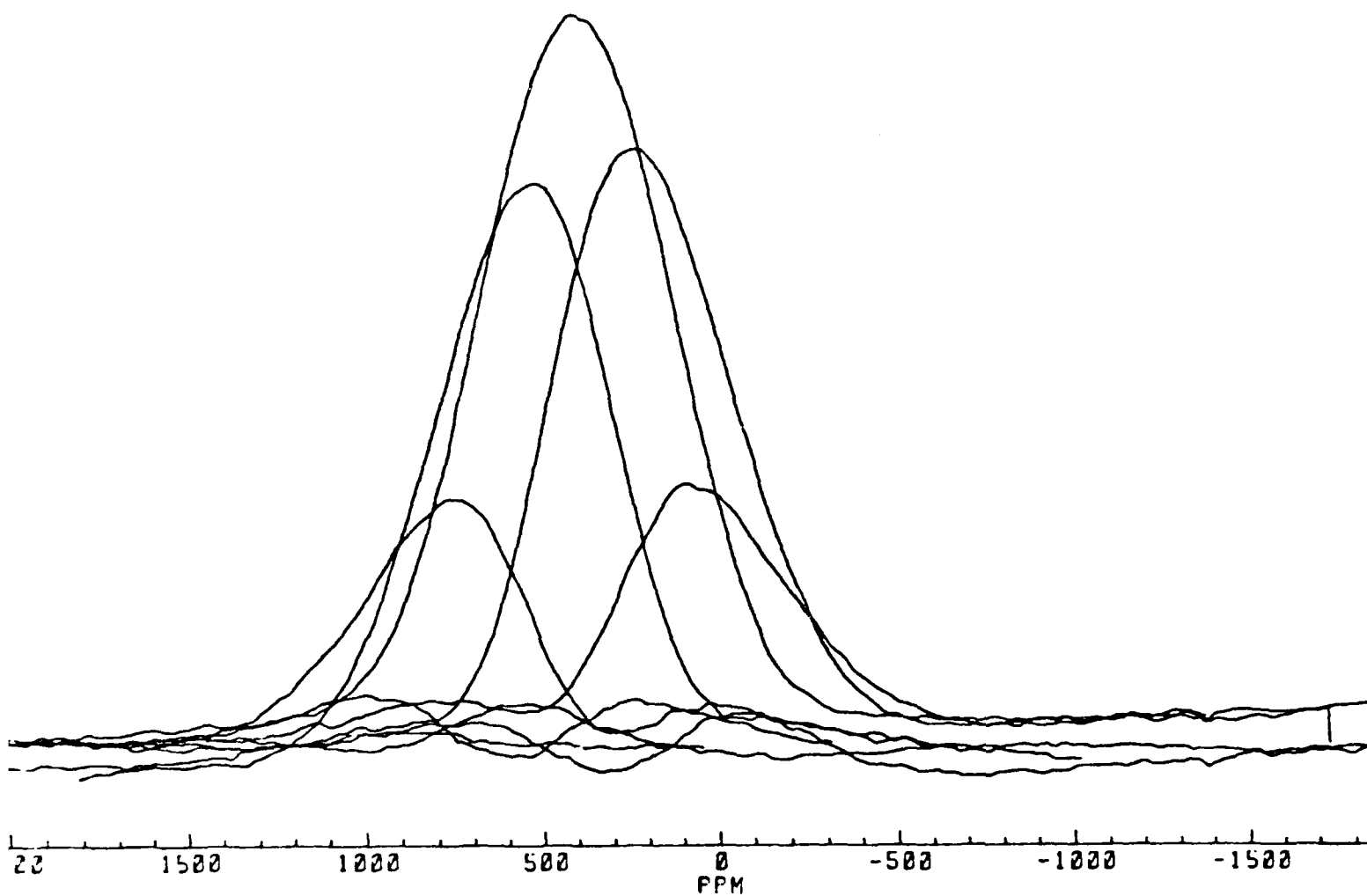PPM

F I G U R E ⑥

YOF , δ ∼ 83 ppm , with MAS .

FIGURE ⑦

EuOF with Static Spin-Echo Mapping .
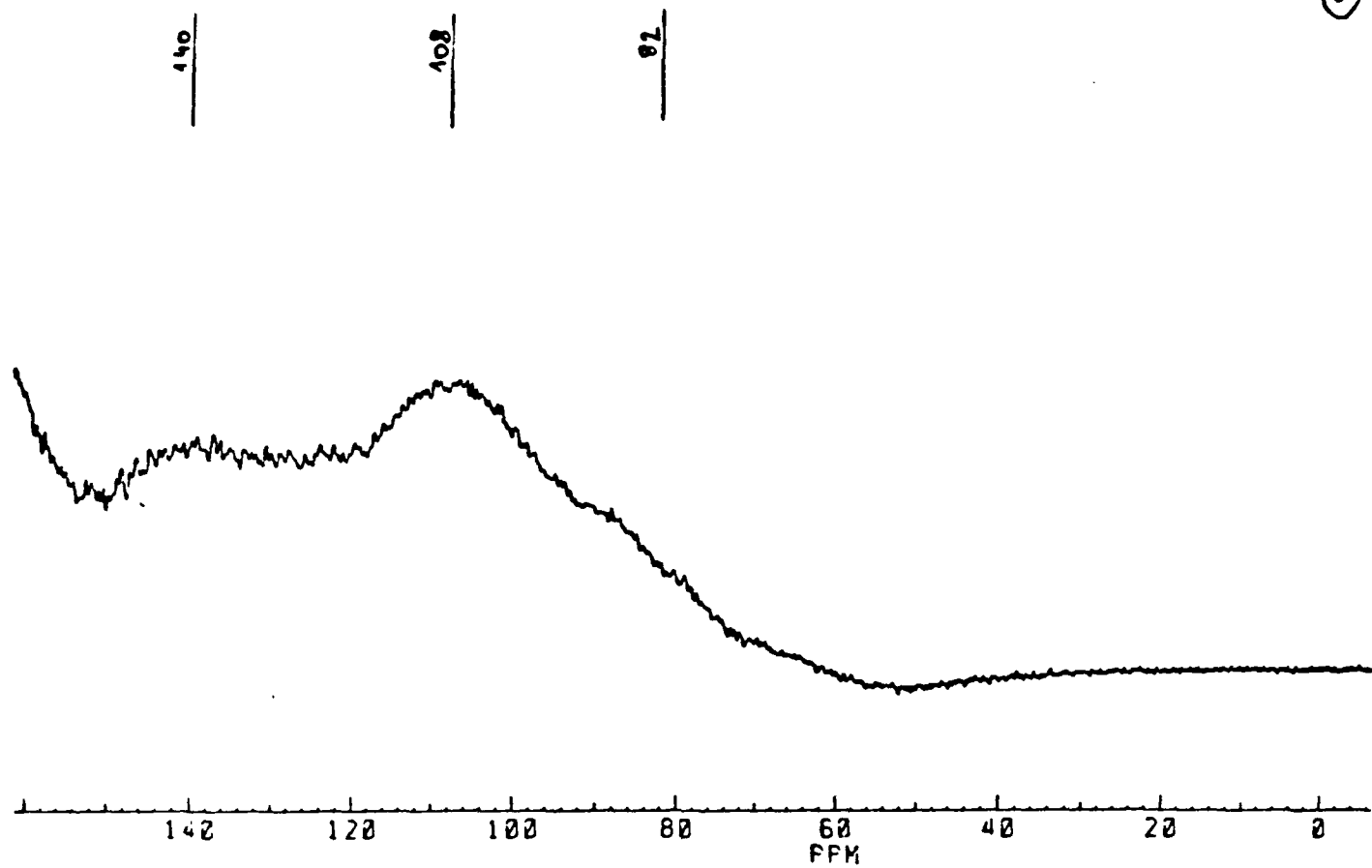
F I G U R E ⑧

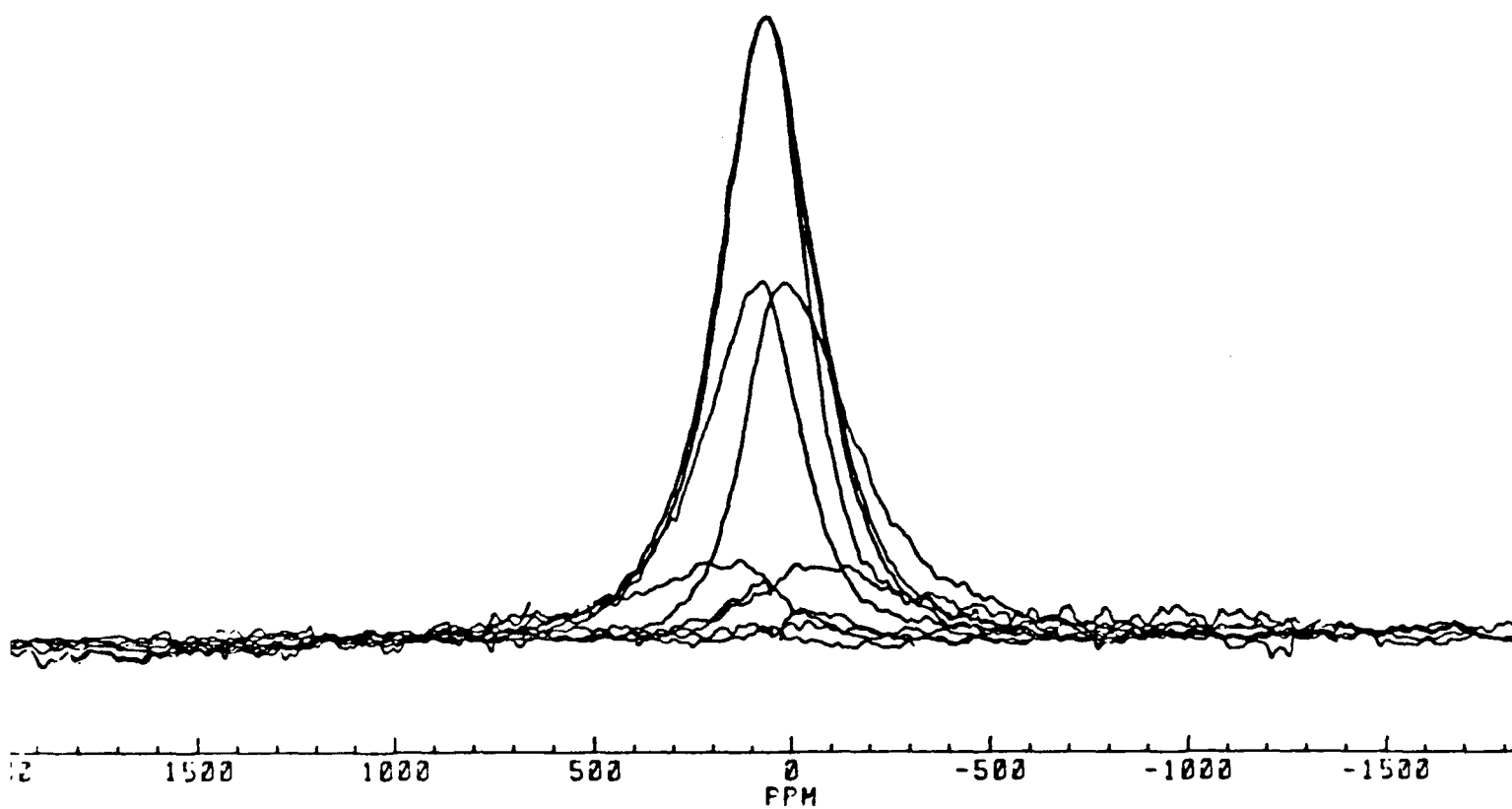Static MPD of YF$_3$; 3 peaks at $\sigma_{11}\sim 140$, $\sigma_{22}\sim 108$, $\sigma_{33}\sim 82$ ppm .

F I G U R E ⑨

CuF_2, $\delta \approx 60$ ppm , with Static Spin-Echo Mapping.